Evidence for magnetic clusters in $BaCoO_3$

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Magnetic properties of the transition metal oxide $BaCoO_3$ are analyzed on the basis of the experimental and theoretical literature available via ab inito calculations. These can be explained by assuming the material to be formed by noninteracting ferromagnetic clusters of about 1.2 nm in diameter separated by about 3 diameters. Above about 50 K, the so-called blocking temperature, superparamagnetic behavior of the magnetic clusters occurs and, above 250 K, paramagnetism sets in.

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Transition metal oxides are among the most studied materials in recent literature. The variety of their physical properties has made them a topic of intensive research during the last few years, the phenomena of colossal magnetoresistance[1] and high temperature superconductivity[2] being the most remarkable. Among them, Co oxides have drawn much attention, since they posses both types of phenomena[3,4]. The magnetic properties of such oxides are a matter of ongoing work. The appearance of properties such as orbital ordering[5], charge ordering[6], spin glass behavior or phase segregation[7,8,9,10,11] makes them very rich in phenomena, whose understanding is a challenge for the scientific community.

$BaCoO_3$ is a transition metal oxide that recently has been a matter of interest of both, experimental and theoretical work[12,13,14,15,16,17]. Its structure[18] can be described as a 2H-hexagonal pseudoperovskite formed by chains of distorted, tilted, and face-sharing CoO_6 octahedra. The plane perpendicular to the chains consists of a hexagonal array of Co atoms, which would lead to frustration for any in-plane collinear antiferromagnetism. The only possible long-range antiferromagnetic state (for collinear moments) could couple ferromagnetic planes antiferromagnetically (so-called A-type structure)[17]. The magnetic properties of $BaCoO_3$ have still not been resolved in literature. It is certain that the Co^{4+} ions are in a low-spin state (S=1/2, $t_{2g}^5 e_g^0$), since an ion with such a high valency produces a large crystal field. This has been shown both experimentally[12] and theoretically[14,15,17]. Moreover, the experimentally found semiconducting behavior[12] has been predicted theoretically[17], using the LDA+U approach, to be a consequence of an orbital ordering phenomenon, which is not yet confirmed experimentally. The actual magnetic configuration of the system is still uncertain. So far no neutron diffraction measurements are available in literature and the experiments that have measured the susceptibility of the system[12] are not conclusive. Theoretical APW+lo LDA+U calculations[17] predict a ferromagnetic state as the magnetic ground state. The most stable antiferromagnetic state is higher in energy but this energy difference is extremely small and depends on the value of U. Therefore any magnetic coupling that might occur will have a very small stabilization energy. This feature is typical for systems showing a cusp in their susceptibility[19], as for $BaCoO_3$.[12]

In this paper, we try to shed some light in the explanation of the magnetic properties of $BaCoO_3$ and resolve an open question in literature. As a start we will analyze the experimental data available and propose a model based on the existence of noninteracting ferromagnetic clusters in the system, which can explain the observations. Then, using ab initio calculations, we will predict the size and density of the clusters, establishing a picture which is fully consistent with both experimental and theoretical data.

When we take a close look at Ref. 12, Fig. 10, we observe susceptibility curves that are typical for a "fine-particle" system[20] with a blocking temperature of around 50 K. This is approximately, where the field cooling (FC) magnetization curve separates from the zero-field cooling (ZFC) one for an applied field of 1 kOe. These FC and ZFC curves indicate that $BaCoO_3$ is formed by regions or clusters, whose magnetic moments are ferromagnetically ordered, but are dispersed into a non-ferromagnetic matrix, a situation that can be described by Wohlfarth's superparamagnetic model[21]. The shape of the FC curve below the blocking temperature indicates that the clusters are widely separated from each other and they do not interact strongly. However, would they interact, this curve would be flat instead of growing exponentially as is observed[20].

The blocking temperature depends on the size of the clusters, the anisotropy constant of the material, the applied field and on the measuring time (on the apparatus utilized for the experiment). By analyzing the data from Ref. 12, one can see that the blocking temperature decreases when the applied field increases. This is the typical behavior of fine-particle systems, even though the contrary might occur if the clusters grow with the applied field[22]. Based on the theory developed by Néel for superparamagnetic particles[23,24], we can predict that the highest blocking temperature (which is reached when the

applied field is much smaller than the so-called anisotropy field) is basically obtained at 1kOe. According to this, the mean blocking temperature varies as:

$$\left(\frac{T_B(H)}{T_B(0)}\right)^{1/2} = 1 - \frac{H}{H_K} \quad (1)$$

where T_B is the blocking temperature and H_K is the mean anisotropy field. From the data in Ref. 12, the blocking temperature is approximately 10 K for H=10kOe and 50 K for H=1kOe. From this, the maximum blocking temperature that can be reached at a very small field is about 53 K, a limit that is basically obtained at a field of 1kOe. This is caused by the large anisotropy of the system, which is due to the quasi-one-dimensional structure formed by widely separated chains of Co atoms. Hence, the value we have chosen to explain the magnetic properties of the system is $T_B \simeq$ 50 K, the expected value for low fields. The description of the system, which will be given below, corresponds to these low applied fields.

From the value of the blocking temperature we can estimate the mean size of the clusters. For doing so, we have calculated the anisotropy constant of the system from ab initio methods. The calculations were performed using the WIEN2k[25,26] software, a package that uses a full-potential, all electron APW+lo[27] method that allows to carry out total energy calculations with one of the most precise methods available. For this moderately correlated transition metal oxide, we used the LDA+U approach including self-interaction corrections[28] in the so-called "fully-localized limit"[29] with U= 5eV and J= 0.5eV, values discussed in Ref. 17. This method has proven reliable for transition metal oxides[30], since it improves over GGA (generalized gradient approximation) or LDA (local density approximation) in the study of correlated electrons by means of introducing the on-site Coulomb repulsion U. The non-orbital dependent part of the exchange-correlation potential was calculated using the GGA in the PBE (Perdew-Burke-Ernzerhof) scheme[31]. Local orbitals (Co 3s, 3p, 3d, Ba 4d, 5s, 5p, O 2s and 2p) were added to obtain a better flexibility of the basis set and to improve the description of the semicore states. $R_{mt}K_{max}$=7 and 500 k-points in the irreducible Brillouin zone (1200 k-points in the whole Brillouin zone) were taken. For calculating the magnetic anisotropy, a fully relativistic calculation was carried out, where spin-orbit effects were included using a second variational scheme[32].

For calculating the energy contribution of the magnetic anisotropy we studied the system in different configurations with the magnetic moments along the different crystallographic directions: (100), (110) and (111), and compared their total energies. The system was studied in a ferromagnetic low-spin state with an alternating orbital order along the c axis as described in Ref. 17, which in this paper was shown to be the ground state. From our total energy calculations, the value of the anisotropy constant is 1.2 mRy per unit cell, which contains 2 Co atoms (about 2×10^8erg/cm^3). This value is larger than the anisotropy energy of a system of fine Co particles ($\simeq 7\times10^6$erg/cm^3). We are not considering the shape anisotropy due to the formation of clusters, but we can assume this contribution to be a secondary effect in this highly anisotropic compound. The lowest energy state has the moments lying in the hexagonal plane (along the b axis). We assume the system to have cubic anisotropy (since the Co ions are in an octahedral environment) and found the value of the anisotropy constant as $K = \frac{E_B}{4}$, where E_B is the energy difference between the easy (b) and hard (c) axis. The procedure for estimating the volume of each cluster is via the following formula for superparamagnetic particles[33]:

$$KV = 25 k_B T_B \quad (2)$$

where T_B is the blocking temperature, V is the mean volume of the cluster and k_B is the Boltzmann constant. The factor 25 comes from the measuring time, which was assumed with a time constant $\tau = 10^2$ s for the experiments of magnetic susceptibility under FC and ZFC conditions in Ref. 12. Using equation 2 with the anisotropy constant calculated ab initio and the blocking temperature from the experimental data in Ref. 12 ($T_B \simeq 50$ K), we estimate that each cluster has a typical diameter of approximately 1.2 nm, containing about 14 Co atoms. The value of the anisotropy constant was calculated at T= 0, hence the volume of the cluster must be considered as a lowest limit. There exists a distribution of particle sizes. This is evident by the fact that the maximum of the ZFC curve is displaced from the point where ZFC and FC curves separate from one another. In our description, we will stick to the average values.

From the blocking temperature (at about 50 K) to approximately 250 K, the system shows a superparamagnetic behavior, entering the normal paramagnetic regime at about 250 K. This superparamagnetism can be due to the presence of magnetic clusters, which can be identified as an assembly of single domain particles with a total magnetic moment of about 14 μ_B per particle (from the ab initio calculations in Ref. 17, the total magnetic moment per Co atom is 1.00 μ_B), where the magnetization of the sample follows the Langevin formula:

$$M = N\mu L(y) \quad (3)$$

where N is the density of clusters per unit volume, μ is the magnetic moment of each cluster, $y = \frac{\mu H}{k_B T}$ and $L(y)$ is the Langevin function. At small y, the magnetization varies linearly with H/T and the Langevin function approximates to a Curie law:

$$M \simeq N\frac{\mu^2 H}{3k_B T} \quad (4)$$

Figure 1 shows the data from Ref. 12 as M vs. H/T. This gives a straight line, that corresponds to the Langevin formula (superparamagnetism) at "normal"

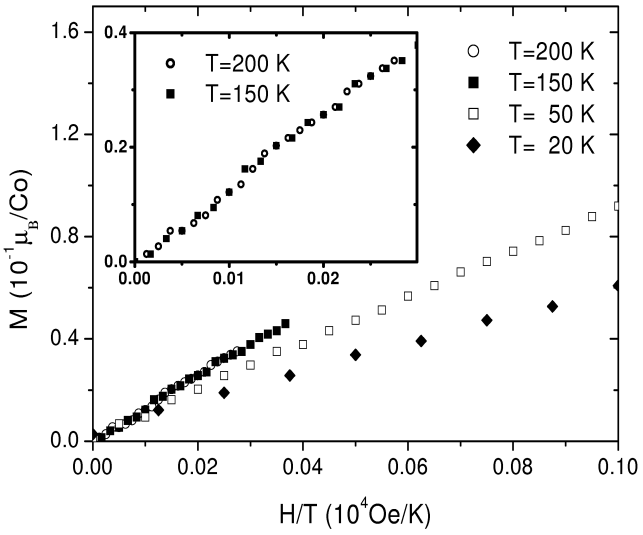

FIG. 1: Total magnetization vs. H/T for four values of the temperature (data from Yamaura *et al.*[12]). In the inset, the curves at T= 150 K and T= 200 K are highlighted, showing an excellent H/T superposition. However, for T$\leq$ 50 K, straight lines have a smaller slope due to the anisotropy effects at temperatures comparable to the blocking temperature.

temperatures (50$\leq$T(K)$\leq$200) and "moderate" fields (0$\leq$H(Oe)$\leq$5$\times$10^4). But, the same type of plot has a different slope for T= 50 K and T= 20 K, because they are below the blocking temperature and the clusters are said to be "blocked" (the effects due to the blocking are appreciable in a region around the blocking temperature, superparamagnetism is observed where ZFC and FC curves match each other, above some 70 K, from the curves in Ref. 12). The slope increases with T and approaches a maximum when T >> T_B, being the difference remarkable in the vicinity of T_B, where thermal equilibrium disappears.

From these curves we have estimated the density of clusters that exists in $BaCoO_3$, being the result that we have one 1.2 nm-diameter cluster in a spherical volume with a diameter of about 3.0 nm. Hence, the average distance between two clusters is about 3 diameters, big enough to assume that they do not strongly interact with each other. As we mentioned above, this fact coincides with the shape of the curves in Ref. 12 that ressemble noninteracting superparamagnetic particles[20].

The normal paramagnetic state appears above some 250 K, when thermal energy is enough to break the magnetic order of the crystal. Below the blocking temperature, $T_B \simeq 50$ K, magnetic moments within the cluster lie along the easy axis and for this system, formed by ferromagnetic clusters, hysteresis loops are expected.

One of the possible mechanism for the formation of these clusters is Nagaev's theory[34,35], according to which a conduction electron might become trapped and polarizes ferromagnetically the antiferromagnetic medium giving rise to the occurrence of ferromagnetic particles dispersed into a non-ferromagnetic matrix, producing a phase separation phenomenon.

In this paper, we have tried to explain the magnetic properties of the transition metal oxide $BaCoO_3$ utilizing ab initio full potential APW+lo LDA+U calculations to interpret the experimental data available. The theoretical prediction of ferromagnetism as the ground state does not coincide with the experimental data of magnetic susceptibility, which is not that of a long-range ferromagnet. The explanation we propose is based on the formation of noninteracting ferromagnetic clusters in the system. Using ab initio calculations, we have estimated the distribution of these clusters. They have a typical size of about 1.2 nm in diameter, and are separated by about 3 diameters, which explains the evidences that they do not interact strongly. With this model, the susceptibility curves can be explained, corresponding to a superparamagnetic behavior in the temperature region from the blocking temperature ($T_B \simeq 50$ K) up to 250 K. Also, the change in the slope of the magnetization vs. H/T curves below 50 K is related to the blocking of the superparamagnetic state. Above 250 K, normal paramagnetism is found.

From our conclusions, $BaCoO_3$ is expected to be an example of a system with a similar behavior to that formed by "ultra-fine" noninteracting magnetic particles and further experimental work is needed to provide more insight into the characterization of the material. SANS (small angle neutron scattering) measurements and in addition a better static and dynamic study of the variation of the magnetization with temperature and applied field is strongly encouraged.

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